

Synthesis and Characterization of Nanocrystalline NiS & Application In Reduction Of Nitro To Amines

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Abstract: The use of Nanocrystalline Nickel sulphide (NiS) as a catalyst in a Hydrochloric Acid solution at 80-90°C to synthesise amines A-H from nitro compounds has been developed. The current approach has the following advantages: global availability, bigger scale synthesis, higher yields, and shorter reaction times.

Key Word: Metal Sulfides; Reduction; Nickel Sulfide; Hydrochloric Acid; Nitro compounds.

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I. Introduction:

Metal sulphide nanomaterials have piqued the interest of researchers in recent years due to their distinct properties in physics and chemistry that differ significantly from those of their bulk counterparts. Because of their unusual quantum size effect and large specific surface areas, these nanoscale metal sulphide materials typically exhibit novel optical, electronic, and magnetic properties. Because of their excellent optical, electrical, and magnetic properties, these materials have a wide range of potential applications in nano devices such as electro luminescence, non-linear optical devices, and photocatalytic material fabrication [1-7].

Transition metal nickel sulphides, represented by NiS and NiS₂, are important materials for studying the physics of a system with strong electron correlation, such as the metal insulator transition, where elucidation of the mechanism responsible for magnetism and electric transport is of great interest [8-10].

NICKEL SULPHIDES: Nickel sulphide, as one of the transition metal sulphides, has attracted a lot of attention because of its unique properties, such as its electromagnetic property involving a first order phase transition from a low temperature antiferromagnetic 20 semiconductor to a high temperature paramagnetic metal, its toughening effect, and its potential applications in fields like IoT[11-16]. Nickel sulphide exhibits complicated, compositional, structural and magnetic phase behaviour. Depending on the synthetic process, a variety of compositions can be obtained including Ni₃S₂, Ni₃+xS₂, Ni₄S_{3+x}, Ni₆S₅, Ni₇S₆, Ni₉S₈, Ni₃S₄, NiS₂, NiS [17-20].

REDUCTION: The loss of an oxygen atom from a molecule or the gain of one or more electrons is referred to as reduction. When one molecule is reduced, another is oxidised, hence a reduction reaction is perceived from the perspective of the molecule being reduced.

Reduction is a chemical reaction in which a substance:

- One or more electrons are gained.
- One or more oxygen atoms are lost, as well as electronegative atoms.
- A hydrogen atom or electropositive atoms are gained.
- An rise in its oxidation number is lost.

NANOSTRUCTURED NICKEL SULPHIDES: SYNTHESIS AND CHEMICAL PROPERTIES: Nickel sulphide has been synthesised through vapor phase reactions, elemental reactions in liquid ammonia, homogeneous sulphide precipitation followed by a sulphiding procedure, and precipitation reaction between metal salts and a sulphiding agent followed by heat treatment in reducing gas [20 - 27]. However, the obtained products typically have relatively large grain sizes, small surface areas, and irregular morphology, which makes them unsuitable for their intended application.

II. Material And Methods

PREPARATION OF NIS NANOPARTICLES:

To render pure NiS nanoparticles, nickel chloride was used as a precursor. For this, 0.75M of nickel chloride was dissolved in 100ml of distilled water and stirred for 30 mins. Drop by drop, 0.8M sodium sulphide was

added to this solution, obtaining a pH of 7. To remove unwanted residues, the NiS precipitate was washed three times with water. It was also washed twice with ethanol to remove impurities. The solution was heated in a hot air oven for 12 hours at 500 °C. The eventually results NiS nanopowder was black in color.

CHARACTERIZATION OF SYNTHESIZED NIS NANOPARTICLES: A field emission scanning electron microscope was used to examine the produced nickel sulphide samples (FE-SEM). A Hitachi S-4160 series instrument was used to capture the FE-SEM pictures. On a Rigaku D/max 2500 V diffractometer with the graphite mono -chromator and Cu target, X-ray powder diffraction (XRD) examination was performed. The FT-IR spectra of nickel sulphide nanoparticles were acquired using the KBr pellet technique on a Perkin-Elmer (spectrum two) spectrophotometer in the wavenumber range of 4000–500 cm⁻¹. At room temperature, the UV–Vis diffuse reflectance spectra were acquired using an Avantes Spectrometer Avaspec-2048-TEC.

III. Results:

FESEM: (Hitachi S-4160 series instrument)

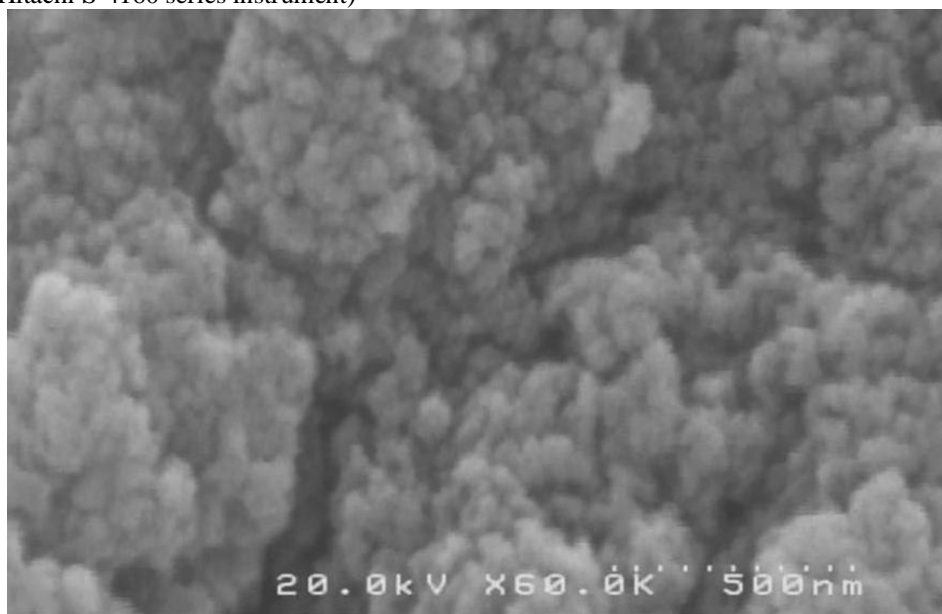


Fig1: FESEM of Synthesized Nickel Sulfide Nanoparticle (NiS) at 500nm

The FESEM pictures in Fig.1 shows the shape of Nickel Sulfide Nanoparticles synthesized using Nickel Chloride & Sodium Sulfide at room temperature.

XRD: (Rigaku D/max 2500 V diffractometer)

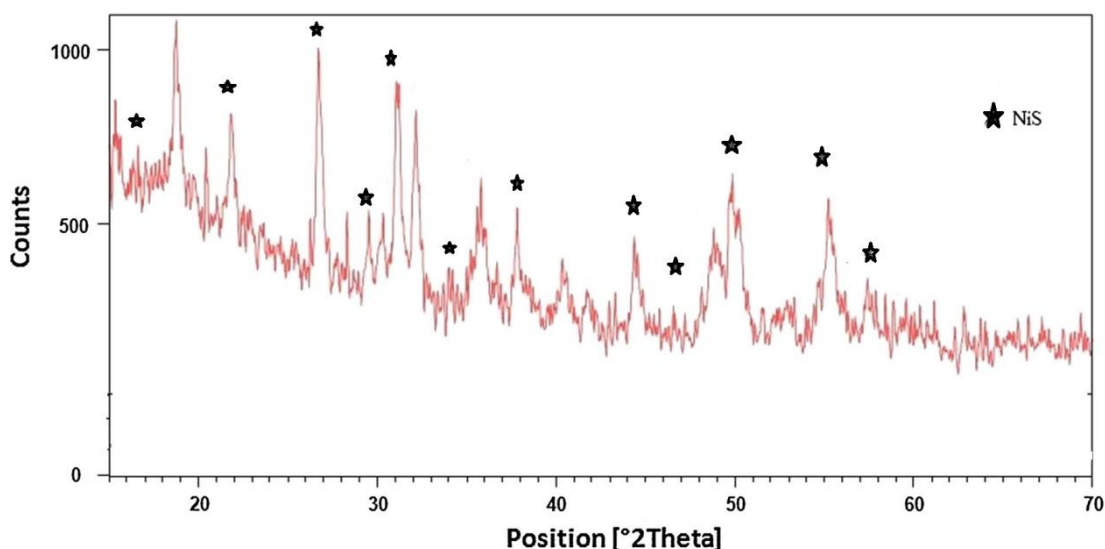


Fig.2 XRD pattern of Nickel Sulfide (NiS) Nanoparticles.

The average crystalline size has estimated from Scherer's formula $d = k\lambda/\beta\cos\theta$ where θ is the peak position angle, λ is wavelength of the X-ray radiation and b is the width of appeared diffraction line at its half-maximum intensity. The results show that the average crystalline size of the obtained nickel sulphide particles (Sample h) varies between 20–45 nm. The optical band gap of NiS calcinated at 200 °C is 4.96 eV the samples show good transmittance.

UV – Spectroscopy: (Avantes Spectrometer Avaspec-2048-TEC)

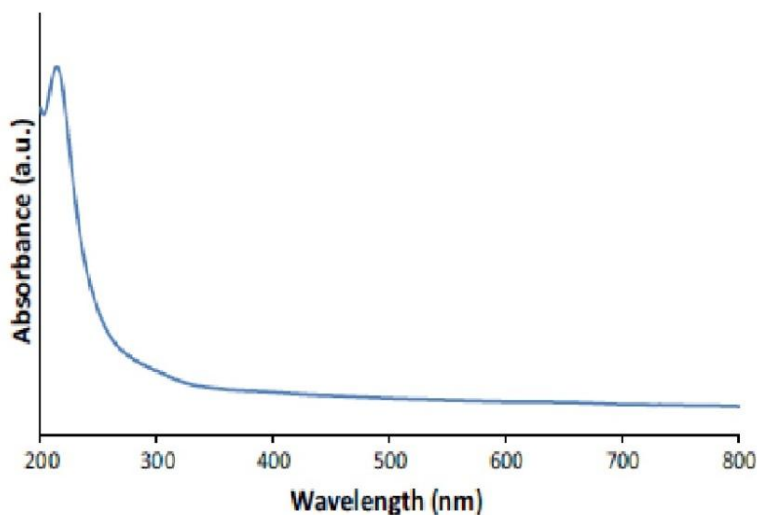


Fig.3 UV – Spectra of Synthesized Nickel Sulfide (NiS) Nanoparticles.

The UV–Vis absorption spectrum of NiS nanoparticles as synthesized can be seen in Figure 3. The formation of nickel sulphide Np's is confirmed by the UV absorption peak observed at 218 nm, which also verifies their narrow particle size distribution and particle homogeneity [28].

FTIR Spectroscopy: (Perkin-Elmer (spectrum two) spectrophotometer)

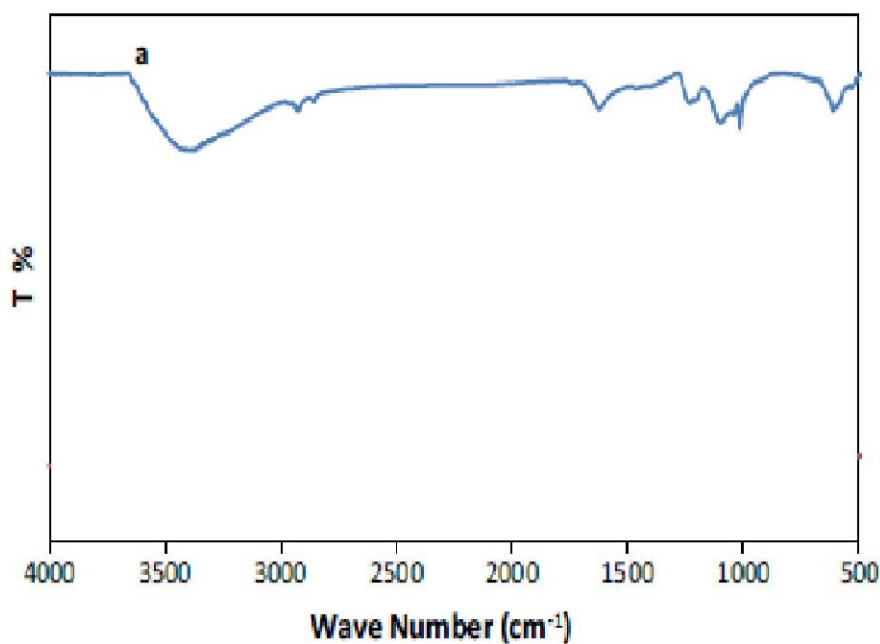
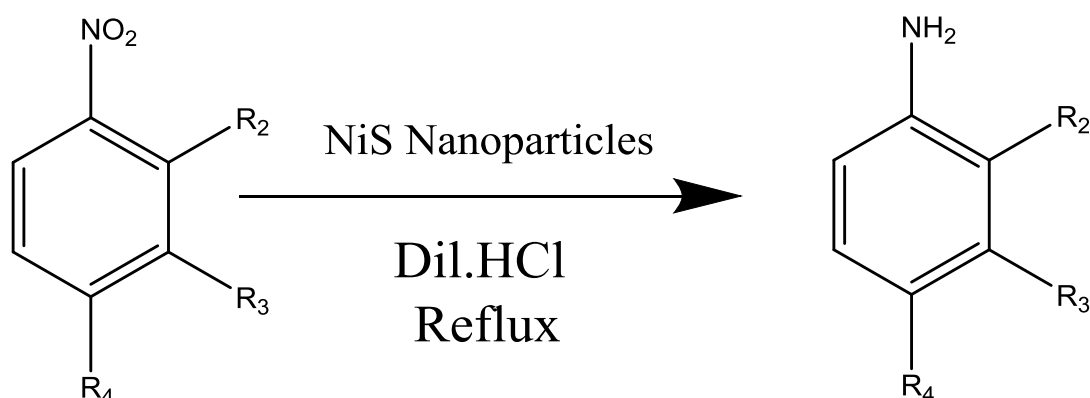


Fig.4 FT- IR Spectra of Nickel Sulfide (NiS) Nanoparticles.

The composition of precipitated nickel sulphide nanoparticles was investigated using FT-IR spectroscopy. Figure 4 depicts the FT-IR spectrum of a nickel sulphide sample generated under ideal chemical precipitation conditions, which reveals minor contaminants. The vibrations in the spectrum were consistent with recent findings on nickel sulphide [29-30]. The absorption of H₂O in the sample and the production of hydrated nickel sulphide nanoparticles are caused by the observed peaks at 3476 and 1675 cm⁻¹. The Ni–S–Ni bending vibration mode is responsible for the peak location of 652 cm⁻¹.

Synthesis of Amines from Nitro Compounds:

A solution of NiS nanoparticles (0.30 mmol) in 20 percent HCl (4 mL) was gently added at room temperature to a solution of nitro arenes (A-H) (0.1 mmol) (Scheme 1). The reaction mixture was refluxed at 80-90 °C. (the reaction was monitored by TLC). After the reaction was completed, the mixture was cooled to room temperature, neutralised with diluted NaOH, extracted with CHCl₃, and dried over anhydrous Na₂SO₄. Under vacuum, the CHCl₃ was eliminated, resulting in high quantities of aromatic amines.



Scheme – 1

IV. Results & Discussion:

According to detailed studies on the reactivity of aromatic nitro compounds (A-H) with NiS nanoparticles to create substituted aromatic amines, the reagent has a significant influence on the reduction processes, as indicated in Table 1.

S.No	R ₂	R ₃	R ₄	Yield	M.P/B.P (°C) found /reported [Ref]
A	H	H	Cl	96%	232 ^o C / 60-70 ^o C [31]
B	H	H	COOEt	97%	172 ^o C / 89.0 ^o – 92.0 ^o C [32]
C	H	H	OCH ₃	97%	243 ^o C / 56.0 ^o – 59.0 ^o C [33]
D	H	COOEt	Cl	95%	295.63 ^o C / 84.0 ^o – 85.0 ^o C [34]
E	H	H	CHO	96%	77.0 ^o – 79.0 ^o C [35]
F	H	H	COOH	94%	340.0 ^o C / 187.0 ^o C [36]
G	H	H	OH	92%	284.0 ^o C / 187.5 ^o C [37]
H	H	H	OCOCH ₃	92%	173.0 ^o – 174.0 ^o C / 73.0 ^o C [38]

Table 1 Analytical data of Synthesized Aromatic Amines from A - H

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